



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 43/00, 41/12, 39/18		A1	(11) International Publication Number: WO 96/28251 (43) International Publication Date: 19 September 1996 (19.09.96)
<p>(21) International Application Number: PCT/AU96/00133</p> <p>(22) International Filing Date: 12 March 1996 (12.03.96)</p> <p>(30) Priority Data: PN 4830 10 March 1995 (10.03.95) AU</p> <p>(71) Applicants (for all designated States except US): MONTECH PTY. LTD. [AU/AU]; Level 1, 30 Collins Street, Melbourne, VIC 3000 (AU). LINFOX TECHNOLOGY PTY. LTD. [AU/AU]; 1 Bowen Crescent, Melbourne, VIC 3004 (AU).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): JAY, William, Harold [AU/AU]; 64 Turana Street, Doncaster, VIC 3108 (AU). BREUER, Paul, Leslie [AU/AU]; 1/7 Monash Street, South Oakleigh, VIC 3167 (AU).</p> <p>(74) Agents: ANGLISS, Michael et al.; Davies Collison Cave, 1 Little Collins Street, Melbourne, VIC 3000 (AU).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: POLYMER SORBENT FOR ION RECOVERY PROCESSES</p> <p>(57) Abstract</p> <p>A process for the selective removal of ions from dispersion of solids in solutions and which also relates to coarse open cell polymeric foams which support ion exchange sites. The process for the selective removal of ions from a solution having solid materials dispersed therein comprises passing the solution having solid materials dispersed therein through a bed of coarse open cell polymeric foam having ion exchange sites. The ion-selective coarse open cell polymeric foam has a cell size sufficient to allow solutions having solids dispersed therein to pass through said foam.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

POLYMER SORBENT FOR ION RECOVERY PROCESSES

The present invention relates to a process for the removal of ions from slurries, pulps or other dispersions of solids in liquids. In particular, the present 5 invention relates to a process for the selective removal of ions from dispersion of solids in solutions and also relates to coarse open cell polymeric foams which support ion exchange sites.

The selective removal of ions from solution is an important process in many 10 industries. In conventional ion recovery or removal processes ions, are removed from solutions by the use of processes such as ion exchange onto solid beads or fibres, membrane processes, activated carbon adsorption, precipitation, solvent extraction, ion flotation and the like. The removal of ions from solutions which also contain solid materials dispersed throughout such as in slurries, pulps and the like 15 is more difficult. The application of ion exchange resins and activated carbon is widely practiced throughout many industries including the minerals processing industry where selective removal of ions from slurries is necessary and has become the method of choice in the recovery of gold by cyanidation and in the recovery of uranium as the uranyl sulphate, for example.

20 In order to achieve good recovery of desired ions from a solution it is desirable to provide a uniform distribution of solid sorbents such as ion exchange resins or activated carbon in the solution. This requires that the density of the solid sorbent be close to the density of the solution otherwise the added ion exchange 25 beads or the activated carbon will sink or float within the solution. Good recovery of ions from solutions having solid materials dispersed therein also requires that the sorption medium is uniformly distributed throughout. In order to achieve efficient recovery of the desired ions it is necessary to provide a sufficient concentration of solid sorbents in the solution, whether or not solid materials are dispersed in the 30 solution. The concentration of solid sorbents is generally limited by the presence of solid particles in solution. For example, the density of the solid sorbents desirably matches or at least approximates the pulp density which is only

determined by the ratio of mass of the solid particles to the solution. The density of the solid particles cannot be modified, nor is it generally possible to significantly change the density of the solution.

5 Extractive metallurgical techniques generally seek to obtain metal values from ores or concentrates. In order to achieve separation, the solids may be introduced into a reactor together with requisite lixivants to dissolve the metal values and in doing so, typically produces a slurry. In such processes, other ions may also be brought into solution. Thus, a material which can selectively remove
10 or recover the desired ion is added to the slurry usually in the form of a solid sorbent dispersed in the slurry. Alternatively, the solution containing the dissolved ions is separated from the solid materials and the metal ions are then recovered or removed from the clarified solution.

15 The maximization of plant capacity in such processes requires a high proportion of solids in the slurry consistent with good mixing and pumping and handling properties. Thus, in order to attempt to distribute the solid sorbents uniformly throughout the slurry, high intensity mixing is often used. This rapid shearing action generated in the reactor can lead to destruction of the active solid
20 sorbent by attrition and breakage. This breakage can result in the loss of valuable ions into the discharge from the plant along with the slurry.

25 The solid sorbent is typically recovered from the slurry or from the solution by screening. In the case of ion exchange resins the particle size of the resin is selected in a size range which is generally fine enough to exhibit desirable loading and elution kinetics. Fine ion exchange beads are more difficult to recover from these pulps because the screen opening size employed must be greater than the particles making up the slurry, but smaller than that of the smallest ion exchange beads. For example, in U.S. Patent 5,198,021 the ion exchange resin bead size is
30 preferentially recommended to be between 6 and 12 mesh. 'Blinding', or screen blocking can thus readily occur.

Additionally, ion exchange resin beads suffer from the problem of osmotic shock. Thus, swelling and shrinkage of the ion exchange resin bead during loading and stripping of the metal ions contained thereon can lead to resin breakage.

5 We have now found that solutions containing solid materials dispersed therein may be passed through coarse open cell polymeric foams having ion exchange sites incorporated into the open cell polymeric foam and the selective removal of ions from solution may be achieved. Accordingly, there is provided a process for the selective removal of ions from a solution having solid materials 10 dispersed therein comprising passing the solution having solid materials dispersed therein through a bed of coarse open cell polymeric foam having ion exchange sites.

Suitable coarse open cell polymeric foams include coarse cell polyurethanes and preferably coarse cell reticulated polyurethanes. Polyurethane-based polymers 15 are recognised for their high abrasion resistance. These polyurethane-based polymers have also been modified to incorporate ion exchanging sites as described in PCT/AU93/00312 and PCT/AU94/00793 incorporated herein by reference and also include any polymeric resin which has been provided with a suitable functionality for the sorption of the desired ion either by interpenetration by a 20 second polymer (such second polymer typically as described in South African Patent ZA 89/2733 and Canad. Patent Application 2,005,259) with or without further chemical modification, polyurethane polymer chemical modification, organic extractant impregnation such as described by Lin *et al* in U.S. Patents 4,814,007, 4,895,597, 4,992,200, 5,028,259, U.K. Patent G.B. 2,186,563A and PCT WO93/19212 25 and Virnig in U.S. Patents 5,198,021 and 5,340,380 or known to those skilled in the application of liquid ion exchange extractants, etc. These polyurethane-based polymers can be produced in a variety of forms such as beads or fibres, but can also be expanded to produce flexible, semiflexible and rigid foams. Blocks of foams several cubic metres in size may be produced. Larger blocks can be produced by 30 well established bonding processes. These blocks of foam can be cut to any suitable shape and size dependent upon the requisite application. Alternatively, blocks of foam can be produced to the desired size and shape by pouring the liquid foaming

reagents into a suitable mould and after the reaction has reached a suitable degree of curing, removing the item from the mould.

The polyurethane foams are preferably flexible and can either be polyester-based or polyether-based. Polyether-based polyurethane foams are generally preferred because of their demonstrated improved chemical resistance over the ester foams. However, for some specific applications ester foams may possess suitable properties. The polyether-based foams may be produced by the reaction under controlled conditions of a suitable polyol or blend of polyols with one or 10 more diisocyanates in the presence of catalysts, cell control agents and, if required, fillers, flame retardants, etc. The polyols are usually based upon the reaction of di- or higher functional materials with ethylene oxide (EO), propylene oxide (PO), or mixtures of these two oxides. For flexible polyurethane foams, glycerine is one preferred starting material and this is reacted with EO and/or PO to produce a 15 polyol with a molecular weight generally in the range of 3000 to 6000. The diisocyanate is generally toluene diisocyanate (TDI) or diphenylmethane-4,4'-diisocyanate-based materials (MDI), but is not limited to these two isocyanates.

Polyurethane foams may be "reticulated", that is, most or all of the residual 20 "windows" or cell walls are removed by such processes as have been described by Volz in U.S. Patent No. 3,171,820 and by Green in U.S. Patent Nos. 3,175,025 and 3,175,030 and which are well known to those skilled in the production or fabrication of polyurethane foams.

25 It has been found that these reticulated polymeric polyurethane foams are able to have solutions comprising solid materials, such as pulps or slurries similar in composition to those found in the minerals processing industry very rapidly pumped through them without any indication of blocking. Fine-celled flexible polyurethane foams under the same conditions are rapidly blocked by the solid 30 materials thus preventing the slurry from continuing to flow freely through the polyurethane foam.

- 5 -

The selection of cell size in the polymeric foam is dependent on the largest particle size of the solid materials contained in the solution. It is preferred that the cell size be at least three times the largest particle size of solid materials in the solution. In the mining industry slurries containing metal ions in solution in 5 addition to solid particulate ore residues are common and we have found it preferable that the polymeric foam has a cell size in the range of from 45 cells per linear inch (180 cells per 100mm) to less than 15 cells per linear inch (60 cells per 100mm). It is desirable to select a cell size wherein the surface area of the polymeric foam is maximized without resulting in blocking of the foam with the 10 solid particles from the solution.

The introduction of these coarse open cell polymeric foams having ion exchanging sites into a reactor in the form of a fixed-bed such as the pachucas used in the gold cyanidation industry provides a process for ensuring that the ion 15 exchanging material is much more uniformly distributed throughout the slurry or pulp and has a large accessible surface area. This means that the solution is able to better contact the ion exchanging sites, overcomes screening problems, reduces the need for intensive mixing and reduces the loss of valuable metal ions to the tailings discharge.

20

Beds of coarse open cell polymeric foams containing the desired ligands may be housed in suitably constructed vessels. Such vessels may be designed to allow liquid containing solid materials to pass through the polymeric foam either by gravity or by pumping or by other means and provides an improved recovery system 25 for the desired ions. Solutions containing from less than 15% of solids to over 50% by weight of solids and varying in particle size from less than 45 micron to greater than 150 micron have been continuously pumped or passed through coarse open cell polymeric foams.

30

Flexible polymeric foams may be able to undergo repeated flexing and therefore the additional possibility of applying a mechanical pulsing action to the foam bed is achieved.

The polymeric foam comprises ion exchange sites. These sites may be provided in the initial manufacturing process of the polymeric foam or may be provided by modification of the foam after its initial manufacture. The selection of appropriate functional groups at the ion exchange sites allows the selective 5 recovery of a broad range of ions in solution. For example the polymeric foam may have ion exchange functionality for the selective removal of heavy metals including arsenic, cadmium, chromium, iron, zinc and mercury; precious metals including gold, silver, platinum, palladium, rhodium, iridium, ruthenium and osmium; other anions and cations including halides, sulfates, nitrates, cyanides, thiocyanates, 10 cyanogen, carbonates and phosphates.

In certain metal ion recovery processes, oxygen may be required as part of the chemical reaction, for example in the dissolution of gold in oxygenated alkaline sodium cyanide solution. These coarse and open cell polymeric foams will allow 15 the passage of both the solution, slurry and if required, air, oxygen or other gas. The polymer foam in some cases may also assist by improving the distribution of the gas throughout the solution, pulp or slurry.

In a second aspect the present invention provides an ion-selective coarse 20 open cell polymeric foam as hereinabove described in which the cell size is sufficient to allow solutions having solids dispersed therein to pass through said foam.

The present invention will be hereinafter described with reference to 25 reticulated polyurethane foams, however, it will be understood that other coarse open cell polymeric foams will be equally suited.

In the gold industry, the loss of gold cyanide by adsorption of the aurocyanide anion onto the surfaces of clays, sulphide minerals, carbonaceous 30 materials, etc. is well recognised and has been termed "preg robbing". The shorter the path length which a metal ion needs to travel to be sorbed by the deliberately introduced selective metal ion sorbent, the less the opportunity for "preg robbing"

to occur. Also, it has been proposed that diluting the pulps to low solids content such as 15% solids content and lower, can also reduce "preg robbing" and thus increase metal ion recovery. The described fixed-bed of ligand-modified reticulated polyurethane foam provides a short path length for the metal ions to travel prior to sorption. Additionally, these modified polymers do not catalyse the oxidation of the sodium cyanide to cyanates or cyanogen as is the case for activated carbon. The slurry pumped to tailings normally contains cyanide, as "free" cyanide or WAD (weak acid dissociable) cyanide, thiocyanates, etc. Thus, the tailings pondage contains anions which are toxic to human, animal and bird life and therefore represent a significant environmental hazard. The presence of these toxic anions may well prevent the return of these sands underground as mine fill because of the potential for the toxic ions to enter the water table.

An example of the industrial application for this technology would be as an alternative for the process as described by Coltrinari in PCT WO87/00072 or the well known AVR and Cyanisorb processes for the recovery of free and WAD cyanide from the CIP or CIL slurry prior to its deposition in a tailings dam. In these processes, the slurry is acidified to provide a solution pH generally between 5 and 8 in order to convert the cyanide species to HCN. Large volumes of low velocity air are then passed through the pH-adjusted tailings in a packed tower to volatilise the HCN. The HCN gas is readsorbed in an alkaline solution and returned to the CIP/CIL circuit. The stripped slurry must have its pH readjusted to 10 to 11 prior to deposition in the tailings dam. This process clearly suffers from a number of disadvantages: the requirement for twice adjusting the pH of the entire slurry and the use of very large volumes of air to volatilise the HCN formed.

The application of a fixed bed of a suitable reticulated polyurethane foam for cyanide recovery offers a number of economic and kinetic advantages as will be described. In the presently described process, the free cyanide is converted to a WAD cyanide such as by the treatment of the slurry with a metal or soluble metal salt in particular with copper or zinc sulphate. The slurry then passes through a suitable bed of a selected reticulated polyurethane foam which has been modified

to contain a suitable ligand. The complex metal cyanide ion is rapidly adsorbed onto the polyurethane foam and the cyanide-depleted slurry passes to the tailings dam without the need for any pH adjustment (other than that which may be required by any particular mining or environmental government regulation 5 applicable to that mine). The loaded polyurethane foam column is acidified to generate HCN gas which is adsorbed in an alkaline solution. A suitable carrier gas such as nitrogen or air may be required. The acid solution may be reused for further stripping. Thus, a closed circuit plant can be designed in which much smaller volumes of air and solutions are required. Alternatively, if a ligand capable 10 of sorbing the WAD cyanide has been used and which is capable of being eluted at high pH, then the WAD cyanide can be stripped from the column. HCN gas can be generated from the strip solution and sodium cyanide formed or alternatively sodium cyanide reformed by electrolysis in a suitably designed electrolysis cell.

15 A further application for the technology would be for the removal of soluble salts in lignite and other coals or for the removal of dissolved metal salts from soils in soil remediation processes, again, by allowing the slurry containing the metal ions to flow through a fixed bed of reticulated polyurethane foam having ion exchange sites to sorb the metal ions.

20

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

25

The following examples are given to describe typical potential applications of this new technology. All percentages are by weight except where otherwise shown.

PRELIMINARY EXAMPLE 1

A slurry was prepared by distributing 40 parts by weight of ground quartz particles in 100 parts of water. 80% of the quartz particles were between 100 5 micron and 150 micron in size, the remainder lay between 45 micron and 100 micron in size. This slurry was pumped both downwards and also upwards through a 1.2 metre high block of reticulated polyurethane foam at particle flow rates in excess of 1 cm per second with negligible pressure drop across the bed.

10 PRELIMINARY EXAMPLE 2

A slurry was prepared by distributing 40 parts by weight of a clay mineral in 100 parts of water. 80% of the clay particles passed through a 75 micron sieve. The slurry was pumped upwards through a 1.2 metre high block of reticulated 15 polyurethane foam at particle flow rates of up to 1 cm per second. Air was introduced into the base of the foam bed and rapidly travelled through it in a vertical direction without substantial pressure drop.

PRELIMINARY EXAMPLE 3

20

Brown coal was mixed with water in a high shear mixer to disperse the fibrous coal particles and to form a slurry containing 30% solids. This slurry was pumped upwards through a 1.2 metre high block of reticulated polyurethane foam containing about 15 cells per linear inch (i.e., 60 cells per 100 mm) at particle flow 25 rates of up to 1 cm per second.

EXAMPLE 1

48.4 grams of a reticulated polyurethane foam containing about 15 cells per 30 linear inch (i.e., 60 cells per 100 mm) was interpenetrated with a mixture of 67 grams of chloromethyl styrene monomer (CMS), 48.5 grams of styrene monomer, 5 grams of divinylbenzene, 2.5 grams of toluene and 0.5 grams of

- 10 -

azobisisobutyronitrile (AIBN) and then cured at 70°C for 24 hours in a nitrogen atmosphere.

The resultant interpenetrated resin was then further reacted by soaking for 5 12 hours at 55°C in a mixture of 1:5 by volume of pyridine:acetone.

The foam treated as described above then was placed in a column and a gold cyanide solution containing 40 percent of quartz to form a slurry was pumped upwards through it. A loading of 41,500 mg Au/kg foam onto this modified 10 polymer was obtained. The quartz particles slurry containing the gold cyanide had the following particle size:

		weight %
	> 150 micron	6.8
15	150-106 micron	57.8
	106-75 micron	25.1
	75-45 micron	9.2
	< 45 micron	1.1

20 No loss in sorption capacity was observed following the pumping of the quartz slurry though this chemically modified reticulated polyurethane foam for 150 hours and no observable building of solid material was recorded.

PRELIMINARY EXAMPLE 4

25

A gold-containing ore (head grade 4.5 ppm) and consisting of quartz (29%), stilpnomalane (14%), chlorite (30%), calcite (5%), muscovite (4%), dolomite (3%), pyrrhotite (10%), pyrite (2%) and minor minerals to 100% was ground to give a P_{80} of 75 micron at a pulp density of 56% and treated with sodium cyanide in a 30 conventional carbon-in-leach plant using a direct injection of oxygen. An analysis of the tailings water showed that it contained 104 ppm of free and WAD cyanide and 360 ppm thiocyanate. The tailings from this gold recovery circuit were passed

- 11 -

over a 150 micron vibrated DSM screen to remove any oversize material and then allowed to flow under gravity through a column 30 cm diameter and two metres high containing a 60 cell per 100 mm reticulated polyurethane foam of density 28 kg/m³. No abrasion was observed after 21 days continual slurry flow.

5

EXAMPLE 2

To the tailings pulp described in Preliminary Example 4 was added on a molar basis sufficient zinc to convert all free cyanide to the complex zinc cyanide 10 anion. This pulp containing metal cyanides was then passed through reticulated and open-celled flexible polyurethane foams (containing either 150 cells per 100 mm or 60 cells per 100 mm) which had been chemically modified to contain approximately 35% of a pyridine-based interpenetrated polymer. The chemical modification was conducted by interpenetrating under nitrogen the reticulated polyurethane foam 15 with a solution containing 100 parts vinylbenzyl chloride, 68 parts styrene, 7.5 parts divinyl benzene, 0.75 parts (AIBN) and 3.7 parts toluene. The interpenetrated polyurethane foam was cured by heating under nitrogen for 18 hours at 80°C in a sealed vessel and then for a further period of 18 hours at 80°C in air. The polymer was then immersed for 12 hours at 50°C in a solution containing pyridine 20 and 20 acetone 100.

After a 2 minute contact with 2.3 g of this polymer in a 16 mm diameter tube (flowrate 47 ml/min.) the slurry exiting the column was analysed. 98% zinc, 83% iron, 87% copper were found to have been removed giving a 95% recovery of 25 WAD cyanide. Once fully loaded with WAD cyanide the polymer was stripped using a 0.1 molar sulphuric acid solution to generate HCN gas which was bubbled through a 1 molar solution of sodium hydroxide to form sodium cyanide.

EXAMPLE 3

30

An acid mine drainage slurry from a copper mine and containing 9.1% quartz and 11 ppm of soluble copper was passed through the column described in

- 12 -

Example 2. The column contained a 60 cell per 100mm reticulated polyurethane foam which had been impregnated with di[2-ethylhexyl] phosphoric acid [D2EHPA]. After 1.5 minute contact time, 53% of the copper was removed from the slurry.

5 **EXAMPLE 4**

A slurry with a maximum particle size of 180 micron and containing 11.9 ppm gold, 11.0 ppm copper, 13.2 ppm zinc, and 14.0 ppm ferric iron all as cyanides, and 0.3 g/l free cyanide at pH 11.0 was passed through the column as described in

10 Example 2 at a flow rate of 90 ml/minute. The column was packed with a 15 cell/inch (60 cells/100 mm) reticulated polyurethane foam which had been impregnated with a gold-selective organic extractant (Aliquat 336 manufactured by Henkel Corp.). After a 1 minute contact time 63% of the gold cyanide, 1% of the copper cyanide, 26% of the zinc cyanide and 4% of the iron cyanide was recovered.

15 This example shows the selectivity which can be achieved according to the process of the present invention.

EXAMPLE 5

20 A slurry containing 10% of solid matter with an average particle size of 100 micron and containing 5.92 ppm of chromium(VI) at pH 2.2 was passed through the column as described in Example 2 with a flow rate of 90 ml/minute. The column was packed with a reticulated and open-celled flexible polyurethane foam (60 cells per 100 mm) which had been chemically modified to contain approximately 35% of a pyridine-based interpenetrated polymer. The chemical modification was conducted by interpenetrating under nitrogen the reticulated polyurethane foam with a solution containing 100 parts vinylbenzyl chloride, 68 parts styrene, 7.5 parts divinyl benzene, 0.75 parts azobisisobutyronitrile (AIBN) and 3.7 parts toluene. The interpenetrated polyurethane foam was cured by heating under nitrogen for 18

25 hours at 80°C in a sealed vessel and then for a further period of 18 hours at 80°C in air. The polymer was then immersed for 12 hours at 50°C in a solution containing pyridine 20 and acetone 100.

30

- 13 -

After a minute contact time 79% of the chromium (VI) was removed. The column once fully loaded with chromium (VI), 91% of the chromium was stripped using seven bed volumes of a solution containing 0.5 molar sodium sulphate and 0.1 molar sodium hydroxide.

CLAIMS

1. A process for the selective removal of ions from a solution having solid materials dispersed therein comprising passing the solution having solid materials dispersed therein through a bed of coarse open cell polymeric foam having ion exchange sites.
5
2. A process according to claim 1 wherein the coarse open cell polymeric foam is a coarse cell polyurethane foam.
10
3. A process according to claim 2 wherein the coarse open cell polymeric foam is a coarse cell reticulated polyurethane foam.
4. A process according to any one of claims 1 to 3 wherein the polyurethane foam is either polyester based or polyether based.
15
5. A process according to any one of claims 1 to 4 wherein the polyurethane foam is polyether based.
20
6. A process according to any one of claims 1 to 5 wherein the cell size of the polymeric foam is greater than 45 cells per linear inch (180 cells per 100mm).
7. A process according to any one of claims 1 to 6 wherein the cell size of the polymeric foam is in the range of from 45 cells per linear inch (180 cells per 25 100mm) to less than 15 cells per linear inch (60 cells per 100mm).
8. A process according to any one of claims 1 to 7 wherein the coarse open cell polymeric foam is in the form of a fixed bed in a reaction vessel.
- 30 9. A process according to any one of claims 1 to 8 wherein the coarse open cell polymeric foam is flexible and able to undergo repeated flexing.

10. A process according to any one of claims 1 to 9 wherein the ion exchange sites of the coarse open cell polymeric foam are suitable for the selective sorption of heavy metals including arsenic, cadmium, chromium, iron, zinc and mercury, precious metals including gold, silver, platinum, palladium, rhodium, iridium, 5 ruthenium and osmium; other anions and cations including halides, sulfates, nitrates, cyanides, thiocyanates, cyanogen, carbonates and phosphates.

11. A process for the extraction of metal values from mineral deposits according to any one of claims 1 to 9 wherein the solution comprises metal ions.

10 12. A process for the removal of soluble salts in lignite and other coals according to any one of claims 1 to 9 wherein the solution comprises soluble salts of lignite and other coals.

15 13. A process for the remediation of soil according to any one of claims 1 to 9 wherein the solution is formed by mixing the soil into an aqueous media.

14. An ion-selective coarse open cell polymeric foam in which the cell size is sufficient to allow solutions having solids dispersed therein to pass through said 20 foam.

15. A polymeric foam according to claim 14 wherein the coarse open cell polymeric foam is a coarse cell polyurethane foam.

25 16. A polymeric foam according to claim 14 wherein the coarse open cell polymeric foam is a coarse cell reticulated polyurethane foam.

17. A polymeric foam according to any one of claims 14 to 16 wherein the polyurethane foam is either polyester based or polyether based.

30 18. A polymeric foam according to any one of claims 14 to 17 wherein the polyurethane foam is polyether based.

19. A polymeric foam according to any one of claims 14 to 18 wherein the cell size of the polymeric foam is greater than 45 cells per linear inch (180 cells per 100mm).

5 20. A polymeric foam according to any one of claims 14 to 19 wherein the cell size of the polymeric foam is in the range of from 45 cells per linear inch (180 cells per 100mm) to less than 15 cells per linear inch (60 cells per 100mm).

10 21. A polymeric foam according to any one of claims 14 to 20 wherein the coarse open cell polymeric foam is in the form of a fixed bed in a reaction vessel.

22. A polymeric foam according to any one of claims 14 to 21 wherein the coarse open cell polymeric foam is flexible and able to undergo repeated flexing.

15 23. A polymeric foam according to any one of claims 14 to 22 wherein the ion exchange sites of the coarse open cell polymeric foam are suitable for the selective sorption of heavy metals including arsenic, cadmium, chromium, iron, zinc and mercury; precious metals including gold, silver, platinum, palladium, rhodium, iridium, ruthenium and osmium; other anions and cations including halides, sulfates, 20 nitrates, cyanides, thiocyanates, cyanogen, carbonates and phosphates.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/AU 96/00133

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl⁹ B01J 43/00, 41/12, 39/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J 43/00, 41/12, 39/18Documentation searched other than minimum documentation (to the extent that such documents are included in the fields searched)
AU, IPC as aboveElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Chemical Abstracts, Volume 88, No. 14, issued 3 April 1978, Cardiff, Wales, UK. M.P. Maloney; G.J. Moody; J.D.R. Thomas, "Extraction and separation of metal ions by foam-supported reagents", page 617, column 2, the abstract No. 98612r, Proc. Anal. Div. Chem. Soc. 1977, 14(9), 244-6 (Eng)	1-5, 8-11, 14-18, 21-23
X	AU, 18629/92 (629790) B (WILLIAM HAROLD JAY) 8 October 1992 See page 1 lines 1-16, claim 1	1-5, 8-11, 14-18, 21-23

 Further documents are listed in the continuation of Box C See patent family annex

• Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
20 May 1996

Date of mailing of the international search report

30TH MAY 1996.Name and mailing address of the ISA/AU
AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION
PO BOX 200
WODEN ACT 2606
AUSTRALIA Facsimile No.: (06) 283 3929

Authorized officer



J. DEUIS

Telephone No.: (06) 283 2146

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 96/00133

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Category of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	WO 94/00237 A (MONASH UNIVERSITY) 6 January 1994 See page 4 lines 3-6, pages 12 and 13, examples 1-2	1-3, 8-11 14-16, 21-23
X	Derwent Abstract Accession No 36928 D/21, Class A97, JP.A. 56-033044 (TOYO RUBBER IND KK) 3 April 1981	1-3, 8-11, 14-16, 21-23
X	FR 2488264 A (LENINGRADSKY INSTITUT TEXTILNOI I LEGKOS PROMYSHLENNOSTI EMENI S.M. KIROV) 12 February 1982. See page 6, lines 11-19	1-3, 8-11, 14-16, 21-23
X	EP 5505 A (BASF A.G.) 28 November 1979. See page 13	1-3, 8-11, 14-16, 21-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/AU 96/00133

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
EP	5505	DE	2820732				
WO	9400237	AU	43000/93	EP	647160	ZA	9304593

END OF ANNEX